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IN SITU U-Th-Pb ISOTOPIC ANALYSES BY EXCIMER LASER ABLATION/ICP–MS ON BRAZILIAN MEGACRYSTAL XENOTIME: FIRST RESULTS OF U-Pb ISOTOPES AT CPGeo-IG-USP.

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INTRODUCTION AND ANALYTICAL CONDITIONS:

The present paper has as main objective to radio frequency (RF) power = 1200 Watts, cooling gas = 15 L/min, aux gas = 0.70 L/min, sample gas flow = 0.75 L/min. Detector configurations: ^{202}Hg = IC_3, ^{204}Hg + ^{204}Pb = IC_4, ^{206}Pb = L_4, ^{207}Pb = IC_6, ^{208}Pb = L_3, ^{232}Th = H_2 and ^{238}U = H_4, where, IC are multi ion counting - MIC and L (low) and H (high) are Multi Faraday Cups. The intensity to ^{80}Ar for stable condition is around 10V (aux gas =0.77 L/min and He gas = 0.65 L/min). The Laser analytical conditions to get the best ablation rate were: wavelength = 193 nm (excimer laser), energy = 7 mJ, repetition rate = 7 Hz, He gas flow = 0.65 L/min, spot size = 29-38 μm.

Representative fragments of MG xenotime were mounted in epoxy disk (2.54 cm or 1inch). For Temora and FC standard analysis a mount previously analyzed by SHRIMP were utilized. GJ reference was mounted in another mount.

DESCRIPTION OF STANDARDS AND SAMPLE

GJ Standard: GJ is a slice of an international megacryst zircon standard. This standard present U concentration around 230±13 ppm analyzed by TIMS) but among 212-422 ppm when measured by in situ analyzes using LA-ICP-MS. Its normal content of radiogenic Pb range from 19 to 37 ppm, and show little common Pb. The ages presented were: $^{206}Pb/^{238}U$ = 599.8±2.4 Ma, $^{207}Pb/^{235}U$ = 601.6±1.9Ma and $^{207}Pb/^{206}Pb$ = 608,5±0.5Ma (Elholou et al. 2006).

Temora Standard: The Temora zircon is extracted from the 417Ma Middledale Gabroic Diorite of the Paleozoic Lachlan Fold Belt of eastern Australia (Woodhead and Hergt, 2005). The results obtained on our research can be seen in the figures 1. All individual analysis are quite concordant giving a mean age of 406±6 Ma (left side). On the other hand if the $^{207}Pb/^{206}Pb$ weighted average is considered the age is 414±17 Ma, therefore, very close to SHRIMP results of 417Ma (right side). In both cases the statistic is bad because the small number of data.

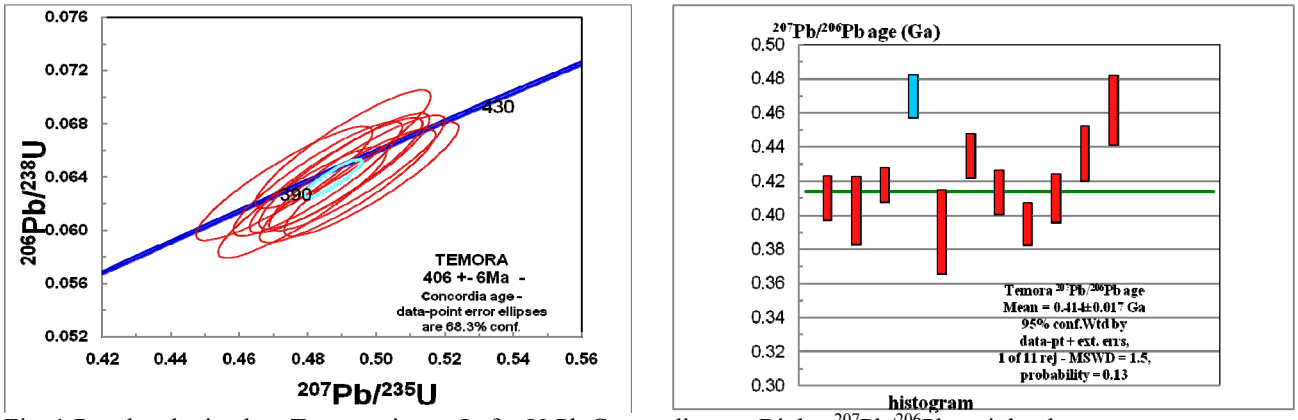

Fig. 1 Results obtained on Temora zircon: Left- U-Pb Concordia age; Right- $^{207}Pb/^{206}Pb$ weighted average age.

FC-1 Duluth Standard: The 1100 Ma FC-1 zircons are derived from anorthositic rocks of the Duluth Complex in north-eastern Minesota (Paces and Miller,1993). It represents a good age standard being used in most SHRIMP laboratories. Our results are shown in figure 2. The U-Pb concordia age obtained is around 1089±10 (left side) but if the $^{207}Pb/^{206}Pb$ weighted average age is considered the value is 1094±25 Ma (right side), therefore, very close to the 1100Ma SHRIMP result.

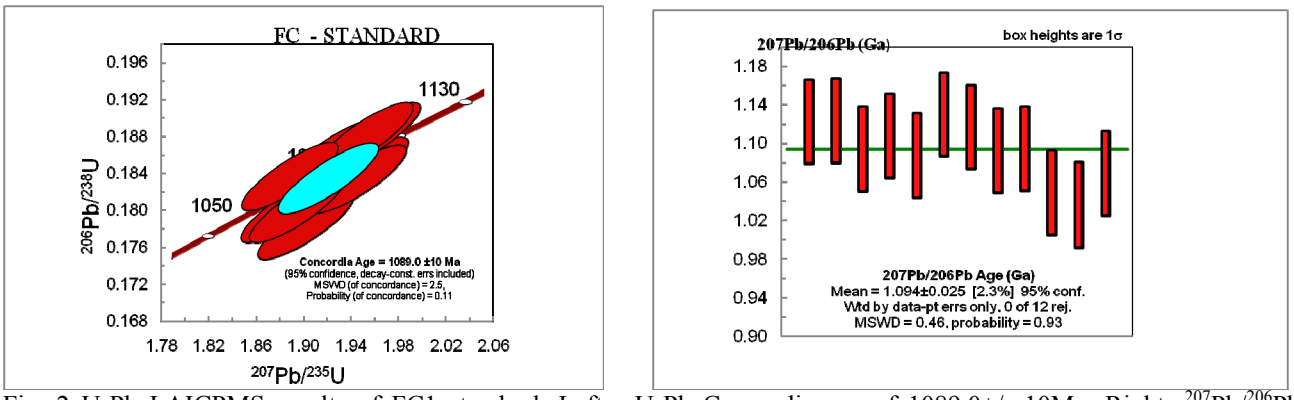

Fig. 2 U-Pb LAICPMS results of FC1 standard: Left - U-Pb Concordia age of 1089.0+/- 10Ma; Right- $^{207}Pb/^{206}Pb$ weighted average age of 1094±25Ma.

Xenotime megacryst (~ 2 x 1 x 1cm) collected from MG (Minas Gerais): The xenotime is a (Y, WREE)PO_4 with Th concentration varying among 300 to 2000 ppm. Common Pb is usually extremely low with $^{204}Pb/^{206}Pb$ ratio <0.0001 what is very good for U-Pb dating. The U-Pb age of 492Ma was obtained by Thermal Ionization Mass Spectrometer - TIMS (Fletcher et al., 2004). Unfortunately preliminary geochemical data show that the crystal is not chemically homogeneous as a good standard should be.

PRELIMINARY RESULTS: The GJ zircon reference show (fig. 3, left side) low ^{232}Th intensity (~2 mV) but high intensity of ^{238}U (150 mV), on the other hand, the xenotime show (fig.3 rigth side) high ^{232}Th intensity (150mV) e normal ^{238}U intensity (90mV), therefore we have very distinct Th/U ratio among zircon and xenotime crystals. A quick comparison between MG xenotime and GJ1 zircon is presented at table 1.

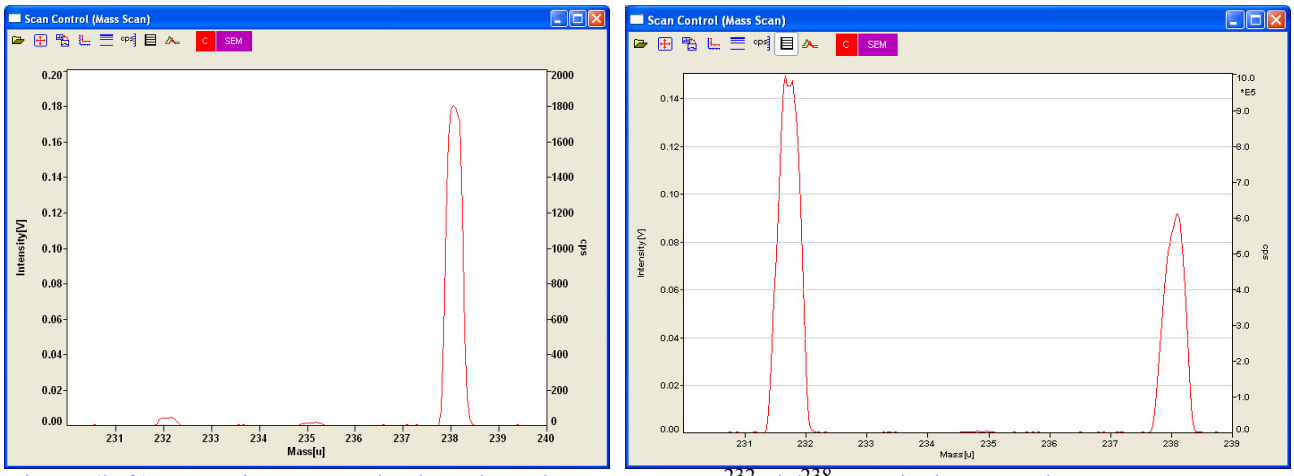

Fig. 3 (left) - GJ zircon standard – Th and U spectrum. $^{232}Th/^{238}U$ ratio is around 0.012 to 0.025 and the ^{232}Th intensity can variety from 0.7 to 3mV (Faraday cup). Fig 3 (right) – MG xenotime fragment - Th and U spectrum from brown crystal fragment by transmitted light (TL). The spectrum show Th/U ratio ~= 1.5, but other fragments change among 0.9 to 4.5, therefore the xenotime fragments are inhomogeneous and 232Th intensity can reach 800 mV for brown fragment (TL).

Table1: Comparison between Xenotime (MG) and Zircon Standard (GJ)

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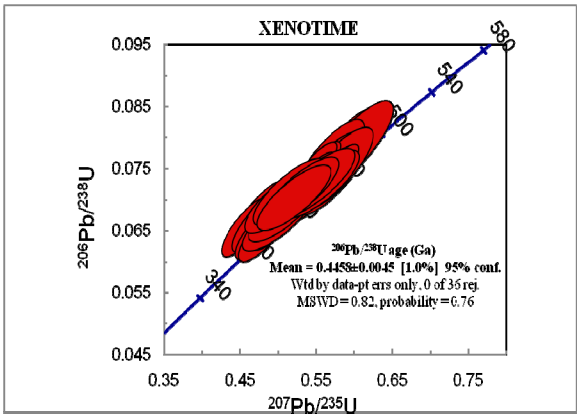
	GJ ZIRCON STANDARD	MG XENOTIME
Main characteristic	($ZrSiO_4$) - High Zr, high Hf and Low WREE	$(Y, WREE)PO_4$. high concentration on Dy_2O_3 (3 – 6%), Er_2O_3 (3-4%), Yb_2O_3 (2-3%) and Lu_2O_3 (0.3 – 0.8%)
$^{232}Th/^{238}U$	0.012 to 0.022 (mean value = 0.017)	0.70 to 4.70
^{232}Th intensity	1.7 - 6 mV (Faraday cup), (4 – 14 ppm)	130 mV (gray, ~300 ppm) to 900 mV (brown, ~ 2000 ppm) by Farady cup
Hf	High intensity (~ 0.7 – 2 V, total current – Farady cup)	Low intensity – detected only in ion counting

The table 1 show that $^{232}Th/^{238}U$ ratio on GJ zircon standard change among 0.012 to 0.022, while MG xenotime fragments variety among 0.7 to 4.7. The ^{232}Th intensity on GJ zircon standard change from 0.7 to 3 mV (measured at Farady cup, see analytical condition above), while MG changes around 130 mV (gray) to 900 mV (brown). Weight REE analyses, using electron microprobe (JEOL - IG-USP) of xenotime fragments indicate high concentration on Dy_2O_3 (3 – 6%), Er_2O_3 (3-4%), Yb_2O_3 (2-3%) and Lu_2O_3 (0.3 – 0.8%).



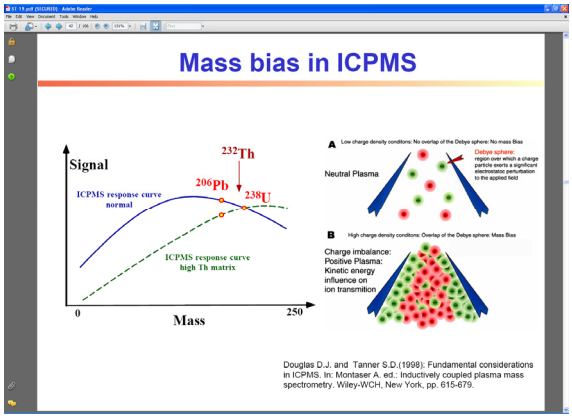


Fig. 4 (left) – The $^{206}Pb/^{238}U$ weighted average age of 445.8 +-4.5 Ma obtained by LA-ICP-MS is slightly lower than the TIMS age of 492 Ma. This lower age is probably due to high ^{232}Th matrix that decrease $^{206}Pb/^{238}U$ ratio and increase $^{207}Pb/^{206}Pb$ ratio. Fig. 4 (right) – Mass bias factor in ICP MS (Douglas and Tanner – 1998). The $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios increase to high Th matrix, therefore, increase $^{207}Pb/^{206}Pb$ age and decrease $^{206}Pb/^{238}U$ age.

The U-Pb results on MG xenotime are shown on figure 4(left side). The xenotime $^{206}Pb/^{238}U$ weighted average age is around 446±5 Ma, therefore quite younger than the TIMS value of 492 Ma which is here explained as due to matrix effect. The figure 4 (right side) presented by Douglas and Tanner (1998) show how the Th influence on U measurement, where, $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios increase in minerals with a high Th matrix, increasing $^{207}Pb/^{206}Pb$ age and decreasing $^{206}Pb/^{238}U$ age.

CONCLUSION

The MG xenotime present a high U content, permitting high intensity beam which is very helpful for the beam focusing during the LA-ICP-MS pre-adjustment set up. Therefore its high REE and Th concentrations, require matrix corrections of several percent for data from most samples. MG also presents variable U and Th abundances in the distincts fragments of the crystal which it is not good for a reference mineral.

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